# Direct measurement of polaron binding energy in $AMnO_3$ as a function of the A site ionic size by photoinduced IR absorption

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Photoinduced IR absorption was measured in undoped $(LaMn)_{1-\delta}O_3$ and $(NdMn)_{1-\delta}O_3$. We observe broadening and a $\sim$44% increase of the midinfrared anti-Jahn-Teller polaron peak energy when $La^{3+}$ is replaced with smaller $Nd^{3+}$. The absence of any concurent large frequency shifts of the observed PI phonon bleaching peaks and the Brillouin-zone-center internal perovskite phonon modes measured by Raman and infrared spectroscopy indicate that the polaron peak energy shift is mainly a consequence of an increase of the electron phonon coupling constant with decreasing ionic radius $\langle r_A \rangle$ on the perovskite A site. This indicates that the dynamical lattice effects strongly contribute to the electronic band narrowing with decreasing $\langle r_A \rangle$ in doped giant magnetoresistance manganites.

The physical properties of manganites with the chemical formula $(Re_{1-x}Ae_x)MnO_3$ (Re and Ae are trivalent rare-earth and divalent alkaline-earth ions respectively) in which giant magnetoresistance (GMR) is observed [1–3] show remarkable changes when the average ionic radius $\langle r_A \rangle$ on the perovskite A site is varied. [4,5] In the region of doping $x$, where GMR is observed, this is reflected in a decrease of the Curie temperature $T_C$ and increase of the size of magnetoresistance with decreasing $\langle r_A \rangle$. [5] The decrease of $T_C$ has been attributed to a decrease of the hopping matrix element between neighbouring Mn sites $t$ as a result of changes of Mn-O-Mn bond angles with $\langle r_A \rangle$. [5]

Traditionally GMR has been explained in the double exchange picture [6] framework, where the hopping matrix element is one of the key parameters influencing directly the Curie temperature. However it has been shown experimentally [7–9] and theoretically [10] that also dynamic lattice effects including Jahn-Teller (JT) polaron formation are crucial ingredients for the explanation of GMR in manganites [10]. In this picture $T_C$ also strongly depends on the electron-phonon (EP) coupling in addition to the hopping matrix element $t$ and any change in the EP coupling as function of $\langle r_A \rangle$ contributes to changes of $T_C$ and other physical properties. Experimentally an increase of the EP coupling with decreasing $\langle r_A \rangle$ is suggested by the shift of the 1-eV polaronic peak in optical conductivity of manganites to higher energy with decreasing $\langle r_A \rangle$ [11,12]. Unfortunately, the peak position of the 1-eV peak does not depend on the polaron binding energy alone [12] and the magnitude of the shift can not be directly linked to change of the EP coupling constant $g$.

Recently we observed a polaronic photoinduced (PI) absorption peak in antiferromagnetic $(LaMn)_{1-\delta}O_3$ (LMO). [13] In this case the peak position is directly linked to the anti-Jahn-Teller polaron [14] binding energy and enables us to *measure directly* the change of the electron-phonon coupling with $\langle r_A \rangle$ in undoped GMR manganites. Here we present photoinduced (PI) absorption measurements in $(NdMn)_{1-\delta}O_3$ (NMO) with $\delta \approx 0$. We observe a $\sim$44% increase of the small polaron energy when $La^{3+}$ is replaced by smaller $Nd^{3+}$. The absence of any concurrent large frequency shifts of the observed PI phonon bleaching peaks and the Brillouin-zone-center internal perovskite phonon modes measured by Raman and infrared (IR) spectroscopy indicate that the polaron energy increase with decreasing $\langle r_A \rangle$ is mainly a consequence of an increase of the electron-phonon coupling constant.

The method of preparation and characterization of ceramic sample with nominal composition $(LaMn)_{1-\delta}O_3$ has been published elsewhere [13,15]. The sample with nominal composition $(NdMn)_{1-\delta}O_3$ was prepared in a similar manner with equal final treatment at 900°C for 300 min in Ar flow [16] to decrease cation deficiency. The X-ray difraction patterns of both samples taken before Ar treatment in 2Θ range 20°-70° showed that both samples are single phase. The samples showed no sign of a ferromagnetic transition in AC susceptibility measurements and we concluded that $\delta$ is sufficiently small that both are antiferromagnetic (AFM) and insulating below their respective Neel temperatures [4,16,17].

PI spectra were measured at 25K in samples dispersed in KBr pellets. CW $Ar^+$-ion-laser light with 514.5 nm wavelength ($h\nu = 2.41$ eV) and optical fluence $\sim$500 mW/cm² was used for photoexcitation. Details of PI-transmitance spectra measurements were published elswhere. [13] Thermal difference spectra [13] (TD) were also measured at the same temperature eliminate possible laser heating effects. Raman spectra were measured at room temperature in a standard backscatering configuration from ceramic powders using a CW $Kr^+$-ion-laser light at 647.1 nm. The scattered light was analysed with a SPEX triple spectrometer and detected with a Princeton Instruments CCD array. The incident laser flux was kept below $\sim$400 W/cm² to avoid laser annealing. [19]

The low temperature ($T = 25$K) PI transmittance ($\frac{\Delta T_{PI}}{T}$) spectra of both samples are shown in Fig. 1. In both samples a strong broad PI midinfrared (MIR) absorption (negative PI transmittance) centered at $\sim$5000 cm$^{-1}$ ($\sim$ 0.62

eV) in LMO and at $\sim 7500$ cm$^{-1}$ ($\sim 0.93$ eV) in NMO is observed.

In the frequency range of the phonon bands (insert of Fig.1) we observe PI phonon bleaching in the range of the 585-cm$^{-1}$ (576 cm$^{-1}$ in NMO) IR phonon band and a slight PI absorption below $\sim 580$ cm$^{-1}$. The PI phonon bleaching in NMO is similar to LMO [13], but shifted to higher frequency by $\sim 20$ cm$^{-1}$ and it consists of two peaks at 620 and 690 cm$^{-1}$ with a dip in-between at 660 cm$^{-1}$. Similarly to LMO this two PI transmission peaks are reproducible among different runs, while the structure of the PI absorption below $\sim 580$ cm$^{-1}$ is not, and presumably arises due to increasing instrumental noise at the lower end of the spectral range. Despite the noise a slight PI absorption below $\sim 580$ cm$^{-1}$ can be deduced from the PI spectra.

The Raman spectra shown in Fig. 2b are consistent with published data. [19] In the 100-900-cm$^{-1}$ frequency range 5 phonon peaks are observed in LMO and 6 phonon peaks in NMO. The frequencies and assignments of the phonon peaks are shown in Table I. The only mode that shifts substantially is the $A_g$ mode that corresponds to the out of phase rotation of the MnO$_3$ octahedra. [19] The mode frequency increases by 17% to 329 cm$^{-1}$ in NMO. [20] The two high frequency modes that are expected to be related to the collective JT distortion [21] shift by less than 5 cm$^{-1}$, which is less than 1 %. Similarly, the frequencies of IR modes shown in Table II do not shift more than 6 % when La$^{3+}$ is replaced with Nd$^{3+}$.

A fit of absorption due to a small polaron hopping given by Emin [32] to the data is shown in Fig. 1 for both samples assuming that $-\frac{\Delta \mathcal{T}_{PI}}{\mathcal{T}}$ is proportional to the absorption coefficient [22]:

$$-\frac{\Delta \mathcal{T}_{PI}}{\mathcal{T}} \propto \alpha \propto \frac{1}{\hbar\omega} \exp\left(-\frac{(2E_{pol} - \hbar\omega)^2}{4E_{pol}\hbar\omega_{ph}}\right) \tag{1}$$

where $\alpha$ is the absorption coefficient, $E_{pol}$ is the polaron binding energy, $\omega$ the incoming photon frequency and $\omega_{ph}$ the polaron phonon frequency. The theoretical prediction fits well to the data with the small polaron binding energies $E_{pol} = 0.34$ eV and $E_{pol} = 0.49$ eV in LMO and NMO samples respectively. The polaron binding energies $E_{pol}$ and polaron phonon frequencies $\omega_{ph}$ obtained from the fit are summarized in Table III.

The polaron phonon frequencies $\omega_{ph}$ obtained from the fit are 310 and 330 cm$^{-1}$ in LMO and NMO respectively and are small compared to the frequencies of the JT related Raman modes at $\sim 490$ cm$^{-1}$. This discrepancy is not surprising, since the width of the peak in (1), from which $\omega_{ph}$ is determined, includes a prefactor which strongly depends on the details of the phonon cloud in the small polaron and is 4 only in a 1D Holstein model, which is a molecular model with a single dispersionless phonon. Taking into account the prefactor as well as dispersion and multiplicity of the phonon branches, $\omega_{ph}$ can be viewed as an *effective polaron phonon frequency* of the different wavevector phonons in the phonon cloud.

The shape of the observed PI absorption peak indicates that the EP coupling is strong and $t > \omega_{ph}$, since otherwise one does not expect to observe a symmetric and structureless peak in optical conductivity. [24] In this case the polaron binding energy is proportional to [23]

$$E_{pol} \propto 2g^2\omega_{ph} + \frac{zt^2}{2g^2\omega_{ph}}. \tag{2}$$

Here $g$ is the dimensionless EP coupling constant, $t$ the bare hopping matrix element and $z$ the number of nearest neighbours. In this formula again $g$ and $\omega_{ph}$ should be viewed as effective quantities corresponding to the combination of different wavevector phonons in the polaron phonon cloud. From formula (2) it is evident that $E_{pol}$ is very sensitive to changes of the EP coupling constant $g$ and $\omega_{ph}$, but depends on the bare hopping matrix element $t$ only in the second order, since in the strong coupling limit $2g^2\omega_{ph} \gg t$.

In our experiment one can see from Raman and IR spectra that, apart from the $A_g$-mode frequency which corresponds to the out of phase rotation of the MnO$_3$ octahedra, all the observed Brillouin-zone-center-phonon frequencies shift by no more than a few percent when La$^{3+}$ is replaced by Nd$^{3+}$. This would at a first sight suggest a link between the $A_g$ octahedral rotation mode, especially because the effective polaron phonon frequencies $\omega_{ph}$ obtained from the fit are very close to the observed mode frequencies. Hardening of the phonon mode by 17% and the $\sim 44\%$ increase of observed small polaron energy would in this case according to (2) imply a $\sim 14\%$ increase of the EP coupling constant $g$.

However, as stated above, the effective polaron phonon frequencies obtained from the fit are extremly inaccurate due to a crudness of the Holstein model and, since the small-polaron phonon cloud due to its localised nature includes mainly large wavevector phonons, the effective $\omega_{ph}$ only weakly depends on the frequency of the zone center phonons. In addition, the observed PI phonon bleaching peaks, which are expected to be directly related to the nonzero wavevector phonons forming the polaron phonon cloud, harden by a mere $\sim 3\%$. We therefore suggest that it is

*very unlikely* that the frequency shift of the $A_g$ mode, which corresponds to the out of phase rotation of the $MnO_3$ octahedra, is directly related to the observed small polaron binding energy shift.

Instead we attribute the *$\sim 44\%$ increase of the polaron binding energy to a $\sim 20\%$ increase of the EP coupling constant g* when $La^{3+}$ is replaced by $Nd^{3+}$ and not to a change of $\omega_{ph}$ and/or the bare hopping matrix element $t$. This is supported by a small shift of the observed PI phonon bleaching peaks and, nevertheless, the negligible shift of the relevant Brillouine zone center phonon modes, especialy the Raman-active high frequency ones, which have been shown to be related to the collective JT distortion [21].

The influence of a decrease of the bare hopping matrix element $t$ with decreasing $\langle r_A \rangle$ on the polaron binding energy can be neglected due to its second order nature in (2), since a decrease of $t$ with decreasing $\langle r_A \rangle$ in (2) would lead to a decrease of $E_{pol}$, which is the *opposite* to what is experimentally observed.

In conclusion, we observe a $\sim 44\%$ increase of the anti-Jahn-Teller polaron binding energy when $La^{3+}$ is replaced by smaller $Nd^{3+}$ in undoped GMR manganites. Absence of any concurent large frequency shifts of the observed PI phonon bleaching peaks and the Brillouin-zone-center perovskite internal phonon modes indicate that the increase of the polaron binding energy is a consequence of increasing electron-phonon coupling strength with decreasing ionic radius on the perovskite A site. This result can be safely extrapolated to doped manganites as indicated by the shift of the 1-eV polaronic peak with decreasing $\langle r_A \rangle$ in optical conductivity of GMR manganites [11,12] and increasing isotope effect of $T_C$ with decreasing $\langle r_A \rangle$ [8].

The decrease of the effective bandwidth resulting in decrease of the Curie temperature $T_C$ and increase of the size of magnetoresistance with decreasing $\langle r_A \rangle$ is suggested to be, not just due to the direct influence of Mn-O-Mn bond angles on the bare hopping matrix element $t$, [5] but also a consequence of the increasing polaronic band narrowing due to increasing electron phonon coupling.

**Acknowledgments**

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TABLE I. The Raman phonon frequencies.

| Mode assignment [19] | $(LaMn)_{1-\delta}O_3$ ($cm^{-1}$) | $(NdMn)_{1-\delta}O_3$ ($cm^{-1}$) | Shift % |
|---|---|---|---|
| $B_{2g}$ octahedra in-phase stretching | 609 | 604 | -0.8 |
| $A_g$ octahedra out-of-phase bending | 486 | 489 | -0.6 |
| $B_{2g}$ O1 along $z$ | 310 | - | |
| $A_g$ octahedra out-of-phase rotation | 282 | 329 | 17 |
| laser annealing induced | 233 | | |
| probably laser annealing induced | - | 248 | |
| probably laser annealing induced | - | 234 | |
| $A_g$ Nd along $x$ | - | 143 | |

TABLE II. The IR phonon band frequencies.

| $(LaMn)_{1-\delta}O_3$ ($cm^{-1}$) | $(NdMn)_{1-\delta}O_3$ ($cm^{-1}$) | Shift % | Comment |
|---|---|---|---|
| 636 | 640 | 0.6 | shoulder |
| 584 | 577 | -1.2 | |
| 510 | 521 | 2.2 | |
| 460 | 482 | 4.8 | |
| 432 | 458 | 6.0 | |
| 418 | 434 | 3.8 | |
| 376 | 392 | 4.2 | |

TABLE III. The small polaron binding energy $E_{pol}$ and the effective polaron phonon frequency $\omega_{ph}$ as obtained from the fit of absorption due to a small polaron given by Emin [32]. The perovskite A site ionic radii for 9-fold coordination [33] ($r_A$) are also given for comparison.

| sample | $r_A(\mathring{A})$ | $E_{pol}$ (eV) | $\omega_{ph}$ ($cm^{-1}$) |
|---|---|---|---|
| $(LaMn)_{1-\delta}O_3$ | 1.216 | 0.34 | 310 |
| $(NdMn)_{1-\delta}O_3$ | 1.163 | 0.49 | 330 |

## I. FIGURE CAPTIONS

Figure 1. Photoinduced absorption spectra of $(LaMn)_{1-\delta}O_3$ (thick solid line) and $(NdMn)_{1-\delta}O_3$ (dashed-line). The thin lines represent the fit of equation (1) to the data. Inset shows photoinduced absorption spectra in the region of the phonon bands. The structure of the PI absorption below $\sim$580 $cm^{-1}$ is not reproducible among different runs, and presumably arises due to increasing instrumental noise at the lower end of the spectral range.

Figure 2. Infrared (a) and Raman (b) phonon spectra of $(LaMn)_{1-\delta}O_3$ (solid line) and $(NdMn)_{1-\delta}O_3$ (dashed-line). The Raman spectrum of $(NdMn)_{1-\delta}O_3$ is offset vertically for clarity.